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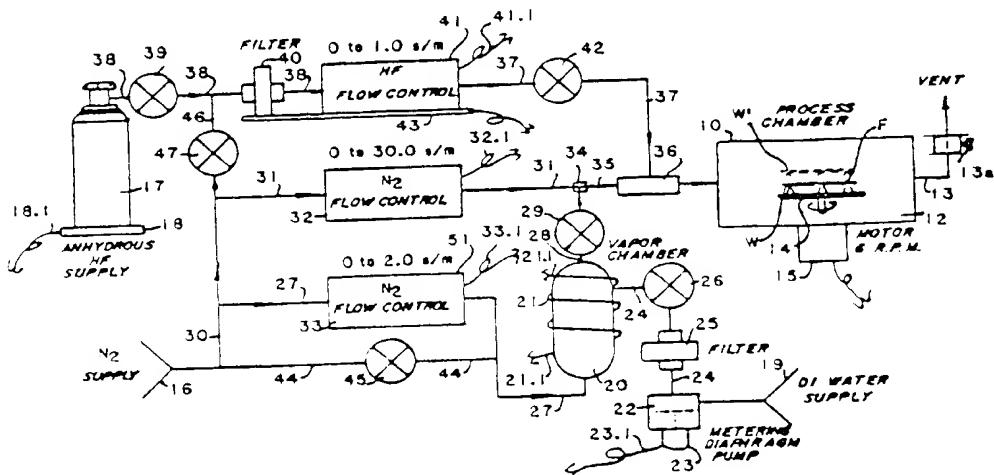
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(54) Title: GASEOUS PROCESS AND APPARATUS FOR REMOVING FILMS FROM SUBSTRATES



### (57) Abstract

source of vapour, over the substrate and film and particularly continuing the flow of the hydrogen fluoride gas over the substrate and film to cause the removal of portions of the film, continuing the flow of the reactive gas over the substrate film for typically 5 to 30 seconds, until a controlled amount of film has been removed, terminating the flow of reactive gas and continuing the flow of dry inert diluent gas to stop the removal of film. In the case of terminating the flow of reactive gas and continuing the flow of the reactive gas and is terminated by hydrogen fluoride gas, the flow of reactive gas is terminated the flow of the reactive gas and is terminated mostly after the removal of a portion of the film, for example, about 10% of the original film thickness, but

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GASEOUS PROCESS AND APPARATUS FOR REMOVING FILMS FROM SUBSTRATES  
BACKGROUND OF THE INVENTION

This invention relates to the process of removing films from substrate materials with reactive gases. More particularly, this invention is concerned with etching substrates (e.g., silicon or polysilicon) to remove from the surface thereof layers or films (e.g., oxides or nitrides of silicon and polysilicons) by action of anhydrous reactive gases, for example anhydrous hydrogen fluoride. The process according to this invention is highly important in the processing of silicon wafers used in the manufacture of semi-conductor integrated circuit chips as well as in other industrial etching and cleaning processes.

Currently, the etching process in the manufacture of semiconductor integrated circuit chips and thin film circuitry has been conducted in a wet acid etching procedure or with plasma techniques. One method of wet etching has been to overlay the surface to be etched with a suitable photoresist mask and to immerse the circuit so masked in a chemical solution which attacks the surface to be etched while leaving the mask otherwise intact. Alternatively, the acid is sprayed onto the surface to be etched. With these known wet etching procedures, etching proceeds at rates at the approximate range of 50 to 2000 angstroms per minute, and is controllable in that range. It has been difficult with the chemical etching processes presently known to achieve well-defined edges on the etched surfaces. The difficulty arises because the chemical action of the wet etchant tends to etch isotropically, i.e., it undercuts the mask by the same distance that it penetrates the underlayer, and thus reduces the final feature dimensions. It is therefore

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An additional problem in wet etching is that at completion of the etching process, thorough rinsing of the wafers is required to remove residual etchant and other contaminants. Accordingly, after the wafers have been etched, they must be cleaned in a separate step, and cleaning contributes to a particulate problem, especially as relates to heavy metals which may be collected on the surface of the wafer. The steps involved in cleaning wafers after etching involve the use of chemicals such as hydrogen chloride and hydrogen peroxide, or ammonium hydroxide and hydrogen peroxide. These cleaning agents must be rinsed from the surface of the wafers subsequent to the cleaning.

In addition, the wet etching of wafers presents other problems which are difficult to deal with. For instance, liquid etchant and rinse media present serious environmental disposal considerations. In most instances these etchant and rinse media must be collected and disposed of in accordance with strict governmental regulations.

In an effort to alleviate these and other problems associated with previous wet liquid etching techniques, various researchers have endeavored to develop gas phase process procedures utilizing a gaseous etchant medium. Known gas phase methods for etching wafers are plasma etching or reactive ion etching (RIE), wherein a vacuum container is filled with a low pressure gas. A surface or substrate to be etched is covered by a photoresist mask and inserted into the container along with the reactive etchant gas. To perform the etching procedure, a voltage is applied to excite the gas, thereby dissociating it and forming various positive and negative ions, reactive neutral species and electrons. The

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dissociated species interact with the surface to be etched producing various gaseous reaction products.

Other efforts have been made to etch with the use of gases, but under extreme or undesirable conditions. They have proved unsuccessful for practical use.

#### SUMMARY OF THE INVENTION

An object of the present invention is to provide a process for gas phase etching or cleaning of substrates for removal of films or layers subject to attack by various reactive gases, and which has the economically and operationally desirable feature of operating near ambient conditions while achieving a controllable, repeatable and uniform result.

Basically the present process comprises exposing of the substrate at near normal atmospheric pressure and room temperature to a continuously flowing atmosphere of anhydrous hydrogen fluoride gas after dry inert gas and water vapor have been flowed over the substrate. For removing a non-hygroscopic film, the flow of vapor continues during the flow of the hydrogen fluoride gas and is subsequently terminated simultaneously with the hydrogen fluoride gas to stop the etch, after which the flow of inert gas continues. In removing a hygroscopic film, the process is the same except that flow of vapor is discontinued shortly before commencing flow of the hydrogen fluoride gas.

In accordance with the invention it has been discovered that mixing an anhydrous reactive gas with the

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conditions. The procedure according to the present invention is used in etching oxide or nitride layers or films of silicon, polysilicon, gallium arsenide, transition metals, aluminum or various silicide films on various materials in the manufacture of integrated circuit chips.

According to the present invention, the substrate to be etched is confined within a process chamber continuously vented to atmosphere as to maintain the pressure in the chamber at "near normal atmospheric pressure". The near normal atmospheric pressure conditions in the process chamber may be actual atmospheric pressure or slightly above atmospheric pressure as may be obtained by utilizing a control device such as a throttle valve at the vent of the chamber. The process chamber pressure may be up to about thirty five inches of water above atmospheric pressure with satisfactory results. The process chamber is maintained at substantially room temperature; and no heating of the process chamber is effected. The substrate having the film or layer to be removed or geometry pattern to be etched is placed in the processing chamber. The process chamber and the system gas flow lines are all purged with a flow of dry inert gas. Then, a mixture of anhydrous reactive gas, dry inert gas and possibly an additional moist inert gas is flowed into the process chamber. The flow of reactive gas causes the etching or removal of the film. The flow is continued in most instances for a time of five to thirty seconds. When etching is completed, the flow of reactive gas is terminated and the reactive gas is purged from the process chamber to stop the etch.

A specific example of reactive gas processing utilizes anhydrous hydrogen fluoride gas for etching

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silicon dioxide films or other etchable films. An inert gas such as nitrogen with a controlled humidity is mixed with the anhydrous hydrogen fluoride gas. This mixture of gases is flowed into the process chamber which is maintained at substantially room temperature and near normal atmospheric pressure conditions. The processing chamber is continuously vented and is thereby maintained at substantially atmospheric pressure. Process chamber pressure will nominally exceed atmospheric pressure by that required to maintain continuous flow against the small back pressure developed by the restriction of the vent. Alternatively by a control device at the vent, process chamber pressure may be increased to twenty five to thirty five inches of water. The moisture in the inert gas initiates and supports the interaction between the anhydrous hydrogen fluoride and the film on the substrate to be etched.

The etching of the film or layer from the substrate is repeatable and controllable in etching a series of substrates and in each substrate, and etching is substantially uniform across the surface of the substrate. The etching is controllable across a wide range of etch rates. As an example, on silicon dioxide, removal rates of from 100 angstroms per minute to 14,000 angstroms per minute have been achieved. The processing chamber may contain a single wafer or multiple wafers being simultaneously processed.

Another aspect of the invention is an improved product formed by the process described herein. The

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improved product has a combination of characteristics not previously found in prior products.

Among the combination of important characteristics are the smooth surface of the silicon substrate upon completion of the etch, and without damage or roughening of the surface due to the etch; the narrow line widths in geometry etching; and the increased level of free fluorine atoms on the surface of the silicon after completion of the etch.

The improved product comprises a filmed substrate having at least a portion of the film removed by exposing the substrate to an anhydrous reactive gas in the presence of moisture and at near room temperature and near normal atmospheric pressure. More specifically the improved product comprises a silicon wafer with at least a portion of its oxide or nitride film removed by exposing the substrate and film to an anhydrous hydrogen halide gas such as anhydrous hydrogen fluoride in the presence of moisture, preferably water vapor carried by dry nitrogen gas or other inert gas.

This improved product and its characteristics provide the advantage of being highly suitable for preparation of high quality circuit chips.

Still another aspect of the invention is a processing apparatus for removing films from substrates. The features of the invention are a continuously vented and openable processing chamber maintained at near room temperature for housing the substrate to be processed. Valved sources of reactive gas such as anhydrous hydrogen fluoride and of purging inert gas such as dry nitrogen

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are connected to the process chamber. A valved source of water vapor is also connected to be carried with at least a portion of the inert gas into the process chamber. Preferably the source of anhydrous reactive gas and its flow control are heated to assure against condensation of the gas.

The processing apparatus provides the advantage of facilitating the selective etching of films from substrates with a minimum of mechanism and under conditions requiring only a minimum of controls. The etching obtained through the use of the apparatus results in an improved product for the production of high quality circuit chips.

#### BRIEF DESCRIPTION OF THE DRAWINGS

In the drawings, FIG. 1 is a schematic diagram of an apparatus for carrying out the process of the invention.

FIG. 2 is a diagrammatic illustration of a substrate with a portion of the etchable film removed according to the disclosed process.

FIG. 3 is a diagrammatic illustration of a substrate with a face from which an etchable film has been removed according to the disclosed process.

#### DETAILED DESCRIPTION OF THE INVENTION

The substrate materials which can be treated by the present process can, generally, be any type of substrate material which will be unaffected by the halogen-containing reactive etchant used.

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manufacture of integrated circuit chips, it will typically be composed of such materials as silicon, polysilicon, garnet, binarys such as gallium arsenide and indium phosphide, also ternarys such as CdHgTe, GaAlAs and GaInP, and quaternarys such as GaInAsP. Other substrate materials which may be treated by this etching, cleaning, and/or polishing process include stainless steel, quartz, aluminum, germanium, gallium and selenium.

Such wafer substrates may be etched one at a time, or a plurality may be etched simultaneously as illustrated in the drawing. An entire boat or carrier of twenty-five wafers may be simultaneously etched in a larger processing chamber.

These different substrates can have films with varying characteristics. The oxide films on silicon wafers may be thermally grown, by application of oxygen under high temperature conditions; or may be vapor generated with steam and oxygen at elevated temperatures; or the film may result from a chemical vapor deposition process. In addition, the oxide films on the silicon wafers may be doped with such materials as phosphorous, arsenic, or boron. These different films may be etched with this invention. It has been specifically found that films doped with phosphorous will etch with this present invention. Most of the work and etching according to the invention has been done in connection with the oxygen and vapor grown films.

It has been found that the thermally grown films are the most dense and have the slowest etch rate, requiring some adjustment in the concentration of the reactive gas in the etching process. The vapor generated films grown in vapor and oxygen at elevated temperatures are common

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films encountered in etching silicon wafers and are considered to be rather typical of the films etched. These vapor generated films are more readily etched at lower concentrations of the reactive gas than are required for etching the thermally grown films. The films produced by chemical vapor deposition are less dense than the usual films encountered and are rapidly etched with low concentrations of the reactive gas.

The doped films are highly etchable with anhydrous reactive gas, such as anhydrous hydrogen fluoride gas and require only dilute concentrations of the reactive gas to accomplish the necessary etching. Such doped films are hygroscopic and may be readily etched without the addition of moisture mixed with the inert gas.

Silicon substrates may have a layer of polysilicon thereon, and the polysilicon may have an oxide film thereon which may be partially or entirely etched away in the same manner as silicon dioxide is etched.

This gaseous treatment invention is also suitable for removing any of the above mentioned materials. For example, quartz boats, which are used to support a multiplicity of wafers in various processing procedures in the manufacture of integrated circuit chips, develop undesirable oxide and nitride layers which must be removed in normal maintenance. One method for cleaning a large number of boats requires a large stainless steel chamber able to accommodate approximately 50 to 60 such boats. The chamber is evacuated, heated to approximately 400°C., and injected with anhydrous hydrogen fluoride, to remove accumulated oxides and nitrides. This prior art process is very slow - the confinement of the

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problems. By providing a process chamber large enough to accommodate these quartz boats, the present disclosed process can easily be used to effect cleaning thereof.

The present process can be used for etching, cleaning and/or polishing any of the above mentioned substrates. For example, this process may be used for preparing the interior surface of glass or silica substrate tubes to be coated for the manufacture of optical waveguides.

The inert gas used in the present process may be any gas which is inert to the materials to be treated and which will remain in the gaseous phase under the process conditions present. Suitable gases include nitrogen, argon, neon, helium, krypton and xenon. A particularly preferred inert gas according to the present invention is nitrogen. It is preferred to use pure nitrogen in the present process, such as chromatographic nitrogen or nitrogen which meets Semi Specifications. Semi nitrogen specifications are as follows:

	<u>Bulk Grade</u>	<u>VLSI Grade</u>
Purity	$\geq$ 99.9987%	99.9994%
CO <sub>2</sub>	$\leq$ 1 ppm	$\leq$ .5 ppm
CO	$\leq$ 5 ppm	$\leq$ .5 ppm
H <sub>2</sub>	$\leq$ 2 ppm	$\leq$ 2 ppm
O <sub>2</sub>	$\leq$ 3 ppm	$\leq$ .5 ppm
THC as Methane	$\leq$ 1 ppm	$\leq$ 1 ppm
H <sub>2</sub> O	$\leq$ 1 ppm	$\leq$ 1 ppm

Proposed particle levels are  $\leq$  20 particles per cubic foot  $\geq$  .2 pm in diameter.

The inert gas is used both in purging the process chamber and the connected system gas lines before and after the reaction procedure, and in diluting the

reactive gas and in preparing the moist inert gas which is mixed with the reactive gas to form the etchant medium. The inert gas may be the same or different inert gas as mentioned above. It is especially preferred in the present process that both the dry and the moist inert gases are nitrogen.

The reactive gas may be derived from any source which will provide a steady flow of anhydrous halogen-containing gas and which will remain in an entirely gaseous condition throughout the reaction system. Hydrogen fluoride is the preferred halogen-containing gas for use in this process. For instance, pure anhydrous hydrogen fluoride may be used as a source. Other sources of HF gas include the following two options: (1) A dilute liquid mixture of hydrogen fluoride and water (with or without ammonium fluoride) may be used as the source of gaseous hydrogen fluoride which readily volatilizes into a gaseous phase. Frequently, such a dilute liquid mixture may be 49% hydrogen fluoride and 51% water, but liquid mixtures containing a smaller proportion of hydrogen fluoride are also available commercially. (2) Bubbling a carrier gas (such as nitrogen) through solutions of various concentrations and temperatures of hydrofluoric acid and/or buffering agents.

An especially preferred source is anhydrous hydrogen fluoride stored as a liquid under its own vapor pressure. It is preferred due to control of reaction rate and uniformity of removal across the wafer surface.

In the drawings, the wafer to be etched is indicated by the letter W and the carrier gas inlet is indicated by the letter C.

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letter F. As has been previously discussed, the films that may be on the face F of the wafer W that will be removed either completely or selectively may comprise silicon dioxide, polysilicon dioxide, silicon nitride, or others as previously mentioned in such instances where the wafer W is formed of silicon or polysilicon.

In FIG. 1 there is illustrated a suitable apparatus for carrying out the process according to the present invention wherein the substrate to be etched is a single face F of a wafer W to be later processed into semi-conductor integrated circuit chips. A housing 10 is openable, to insert and remove a wafer W for etching, and closeable to form a sealed process chamber 12. Exhausts 13 are provided in the housing 10 of the process chamber 12 and are normally vented open to the atmosphere to allow for exit of the purging gas and the etching gas during the various phases of the process. The exhausts 13 are sufficiently open as to avoid creating any significant back pressure in the process chamber, but may incorporate a controllable throttle valve 13a to slightly throttle the gas flow and to slightly raise the pressure in chamber 12. The housing 12 may be constructed of any material which will be inert to the etchant gas under the process conditions. Suitable materials include, for example, stainless steel, ultra high molecular weight polyethylene, polypropylene, Teflon PFA, a trademark of E.I. DuPont DeNemours of Willmington, Delaware, for a plastic known as a perfluoroalkoxy. An especially preferred material for the housing is the Teflon PFA or the ultra high molecular weight polyethylene.

The wafer W is supported on a horizontal turntable 14, so that its upper face F, which is being subjected to cleaning or etching is entirely free, clear and

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unobstructed. The turntable 14 is powered by a variable speed motor 15, which may be adjusted according to individual process conditions. Speeds of between about 1 and about 15 rpm are suitable, and a speed of about 6 rpm is preferred. Additional wafers W shown in dotted lines may be carried on the turntable for simultaneous etching.

A source of dry nitrogen 16 is provided, and it is important that the nitrogen source be of ultra high purity, for example, bottled chromatographic grade dry nitrogen. The source of nitrogen 16 is maintained at room temperature.

A source of gaseous hydrogen fluoride 17 is also provided. The hydrogen fluoride source may be supplied as a liquid in a cylinder, and then evaporated at a temperature sufficient to insure free flow of the gaseous hydrogen fluoride from the source. Alternately, instead of using a technical hydrogen fluoride, which is regarded as 99.99% pure, the anhydrous hydrogen fluoride, may be derived from bottled hydrogen fluoride which is 49% hydrogen fluoride and 51% water, suitably heated to drive off anhydrous hydrogen fluoride for use in the present process. A heating element 18 is provided beneath the bottle of hydrogen fluoride 17, or the heating element may wrap around or embrace the bottle of hydrogen fluoride. Heater 18 is connected to a control circuit 18.1 which supplies electrical energy to the heater and controls the temperature of the heater. The source of hydrogen fluoride is maintained at a suitable temperature as to be assured that the hydrogen fluoride is maintained in anhydrous gaseous condition. Accordingly, the supply anhydrous hydrogen fluoride is maintained at about 17°C.

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A source of water 19 for vapor generation is provided. The water source 19 should be of high purity, for example, deionized water.

An important component of the vapor generation system is a vapor chamber 20. In an especially preferred embodiment, the vapor chamber 20 is approximately 1000 ml in volume, constructed of stainless steel. Around the outside of this vapor chamber 20 is a heating element 21 which allows heating of the vapor chamber 20 to any desired process temperature. Generally, the operating range for the vapor chamber 20 is in the range of about 45°C. to about 120°C. The heating element has electrical connections 21.1 extending therefrom and supplying electrical energy to the heating element and regulating the heating of it as to maintain the desired temperature in the vapor chamber.

Water to be vaporized is supplied into vapor chamber 20 through a metering diaphragm pump 22, operated by a solenoid 23. Solenoid 23 which controls operation of the metering diaphragm pump is connected to a control circuit 23.1 so that the operation of the diaphragm pump can be coordinated with the operation of the other portions of the system. The flow line 24 for the deionized water carries the metered water through a filter 25 and then to a control valve 26. The flow line 24 communicates with the interior of the vapor chamber 20 so that with each operation of the diaphragm pump 22 a spray or jet of water is directed into the vapor chamber 20. As the water is sprayed or jetted into the vapor chamber 20, the water is broken up into small droplets and subjected to the heat from the heater 21. A small quantity of nitrogen, carried into the vapor chamber 20 through a flow line 27 mixes with the water vapor formed in the

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vapor chamber 20 and serves to carry the water vapor out of the vapor chamber and into the flow duct or tube 28 for mixing with the dry nitrogen from source 16. Any portion of the spray of water not immediately put into vapor form will be collected during the cycle in the bottom of chamber 20 and the nitrogen from line 27 will bubble through it to add vapor into the flow.

Nitrogen is supplied into the flow line 27 from the nitrogen supply 16 which is connected to a manifold line 30. Nitrogen is supplied through the manifold line 30 to the branch line 27 for the vapor chamber 20 and also through another branch line 31. Nitrogen flow controls 32 and 33 are interposed in the flow ducts 31 and 27 respectively for regulating the flow of nitrogen through these lines. These flow controls may be adjusted to operate at various percentages of rated capacity from zero percent to one hundred percent, and may be supplemented by on-off valves in series. The flow control 32 has connection to a flow control circuit 32.1 which regulates flow through the flow control 32; and the flow control 33 also has connection to a flow control circuit 33.1 by which the flow through the flow control 33 is regulated. The flow control 32 operates throughout a wide range of flows, from 0 to 30.0 slm (standard liters per minute). The flow control 33 operates in the low range of flow of the nitrogen gas, from 0 to 2.0 slm.

The flow line 28 from the vapor chamber 20 is connected to the flow line 31 at a standard tee fitting 34 for mixing the moisture laden nitrogen from vapor chamber 20 with the dry nitrogen flowing from the flow control 32 and through line 31.

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control 32 is mixed with the moisture laden vapor from the vapor chamber 20. The mixed dry and moist nitrogen is carried into a supply line or tube 35 and into a mixing device 36. The mixing device 36 may be any of a number of types of devices, but it has been found an aspirator operates satisfactorily for mixing the inert gases, carrying vapor, with anhydrous reactive gas supplied through the flow line 37 which is connected into the aspirator 36.

The reactive gas in the flow line 37 will be in some cases anhydrous hydrogen fluoride from the source bottle 17. The flow line 38 from the supply bottle 17 is connected through an on/off valve 39 and through a filter 40 for supplying anhydrous hydrogen fluoride gas to the flow control 41 from which the measured amount of anhydrous hydrogen fluoride gas is flowed into the flow line 37 which contains another on/off valve 42. The flow control 41 is similar to flow controls 32 and 33 with the exception that the flow control 41 is adjusted to operate within a range 0 to 1.0 slm. The flow control 41 is connected to a circuit 41.1 which controls the flow of gas through the flow control and through the ducts 37 and 38.

The flow control 41 and the filter 40 and the flow line 38 between the flow control and the source bottle 17 of anhydrous hydrogen fluoride are all heated to maintain the anhydrous hydrogen fluoride gas in gaseous and anhydrous condition. The heating of these parts is produced by a heater plate 43 upon which the flow control 41 sits and upon which the filter 40 also sits. The filter 40 and the flow control 41 are heated and they conduct the heat to the flow lines 38 to maintain the hydrogen fluoride gas at desired temperature. The flow

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lines 37 and 38 are preferably short as to minimize the possibilities of condensation of the anhydrous hydrogen fluoride gas.

A nitrogen flow line 44 with an on/off valve 45 therein is connected into the flow line 27 between the vapor chamber 20 and the flow control 33, and is also connected into the nitrogen manifold line 30 for providing a purging shunt around the flow control 33.

Another flow line 46 is connected into the flow line 38 between the filter 40 and the valve 39 and is also connected into the nitrogen manifold 30, and incorporates an on/off valve 47 so that substantial volumes of nitrogen may be shunted through the flow control 41 and line 37 for purging this portion of the hydrogen fluoride flow system.

Alternative methods of generating a water vapor in the vapor chamber 20 may be used with equally desirable results. For example, an ultrasonic nozzle which uses a high frequency vibration to break up the stream of water passing through the nozzle into very fine water droplets may be used to generate the required vapor. Another alternative method of generating the water vapor is to aspirate a high pressure stream of water through a very small orifice nozzle into the vapor chamber 20. It will be understood that the water vapor produced by these alternatives need not be heated as in the preferred mode described. Another alternative for producing the vapor is to maintain a deionized water bath, unheated, or heated to temperatures in the range of 45°C to 120°C and then small quantities of dry nitrogen trickle or

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up moisture, carrying moisture along to the mixing device 36. Such a bath may be long and narrow, with a surface area of approximately twenty four square inches or more.

In general, the etching process is carried out by mixing small quantities of anhydrous hydrogen fluoride gas with substantial quantities of dry inert nitrogen gas which acts as a diluent for the anhydrous hydrogen fluoride gas, and also mixing small quantities of vapor laden nitrogen. The mixed gases are flowed into the process chamber 12 as to expose the film on the face F of the wafer W to the dilute reactive gas, and the small quantities of water vapor causes the reaction between the oxide film and the anhydrous reactive gas to be initiated and sustained through duration of the etch. The etching continues for from five to thirty seconds and the exhaust 13 is continuously opened to vent so that gases are continuously flowed out of the process chamber as well as into the chamber. Although the small quantities anhydrous reactive gas and of the vapor laden nitrogen are both at temperatures somewhat above room temperature, the much larger quantities of dry nitrogen from the flow control 32 are at substantially room temperature so that the temperature in the process chamber is near room temperature during the etch process. While it is not considered essential that the wafer be rotated during the etch process, the rotation of the wafer is preferred unless thorough diffusing of the gases flowing through the chamber can be otherwise assured.

More specifically, at the beginning of a process cycle, a wafer W is placed in the process chamber which is thereafter closed, but continuously maintained open to the vent. Purging quantities of dry nitrogen are flowed through the mixing device 36 and through the process

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chamber 12 to clear other gases and contaminants from the process chamber; and purging nitrogen is also flowed through the on/off valve 47, filter 40, flow control 41, and flow line 37 as to purge all of the hydrogen fluoride gas from this part of the system and to assure that no liquid droplets remain in the system. Simultaneously substantial quantities of purging dry nitrogen are flowed through the flow control 33, and through the shunt line 44 into the vapor chamber 24 for purging all moisture and vapor from the vapor chamber 20 and the flow line 28, and of course as the purging by the nitrogen continues, all moisture and contaminants are removed from the processing chamber 12.

When the purging of the lines has been completed, valves 47 and 45 are closed, and small quantities of nitrogen will continue to flow through the vapor chamber 20. The metering diaphragm 22 is operated through a single cycle as to spray a small quantity of deionized water into the vapor chamber 20, as to be heated, vaporized and mixed with the flowing dry nitrogen therein and to be carried from the vapor chamber to the tee fitting 34 for mixing with the flowing dry nitrogen from flow control 32.

Immediately after the diaphragm pump 23 is operated as to commence the generation of a vapor in chamber 20, the on/off valve 39 is opened to flow the anhydrous hydrogen fluoride gas through heated flow lines and through the heated flow control 41, thereby supplying anhydrous hydrogen fluoride gas into the mixing device 36 whereupon the anhydrous hydrogen fluoride gas is mixed with small quantities of moisture and with substantial

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applied onto the face of the wafer by flowing the gases through the chamber and over the wafer as the wafer is being revolved. After a suitable lapse of time during which etching continues at near normal atmospheric pressure, flow of the hydrogen fluoride and water vapor is terminated by closing valves 39 and 42 to stop the flow of hydrogen fluoride gas, and valve 29 to stop the vapor flow, while the flow of dry nitrogen from flow control 32 is continued. The process chamber 12 is purged of hydrogen fluoride to quickly stop the etching process; and the valve 45 is opened as to complete the purge of the vapor from the vapor chamber 20.

More specifically, it will be understood that the flow controls 32, 33 and 41 are all mass flow controllers and control the flow by mass.

In the carrying out of the process with the apparatus illustrated, and in etching the oxides worked with, flow control 33 is typically operated at forty percent of its capacity, producing a flow rate of approximately 0.8 slm. In each etching process, during which the face of one wafer is exposed to the etchant mixture, approximately 0.25 cc to 2.0 cc of deionized water is metered by the diaphragm pump 22 and sprayed into the vapor chamber 20. Typically, approximately 0.5 cc to about 1.5 cc of the deionized water is metered by the diaphragm pump and sprayed into the vapor chamber during each etching cycle. It is important that the flow of vapor-laden nitrogen from the vapor chamber 20 be continued all during the time during which the anhydrous reactive gas is flowing, and accordingly, care is taken to be assured that vapor-laden nitrogen is flowing from the vapor chamber for mixing with the dry nitrogen at a

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time prior to commencing flow of the anhydrous hydrogen fluoride gas and until the flow of the hydrogen fluoride gas is terminated.

It has been found that improved control in the rate of etch and the total etching is achieved by pretreating the silicon wafer with vapor, prior to introducing anhydrous hydrogen fluoride into the process chamber. Preferably, the vapor laden nitrogen has picked up vapor by passing the nitrogen through a closed spaced above and over a water bath. The processing chamber is first purged with dry nitrogen gas; and during the purge, the vapor laden nitrogen is introduced into the processing chamber for pretreating the film on the substrate or silicon wafer. The pretreatment of the film with the vapor laden nitrogen causes small quantities of the moisture to be adsorbed into the film although the film would not ordinarily be regarded as hygroscopic. By this pretreatment of the wafer and film, a uniform condition is created across the entire face of the film. After the pretreating of the wafer, flow of anhydrous hydrogen fluoride is commenced to start the etching phase. When an appropriate etching time has elapsed, the flow of anhydrous hydrogen fluoride and the flow of moisture laden nitrogen are stopped simultaneously, while the flow of dry nitrogen is continued to terminate the etch and purge the processing chamber.

If the film on the wafer is of a more conventional hygroscopic nature as to adsorb a considerable amount of moisture, the pretreatment will vary slightly from the pretreatment of the ordinary oxide film as described in the paragraph above. In processing the wafer with the

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nitrogen is also introduced into the processing chamber as to saturate the hygroscopic film with moisture. The vapor laden nitrogen will apply a small amount of excess moisture on the face of the film. After a few seconds of this pretreatment by the introduction of moisture laden nitrogen, the flow of moisture laden nitrogen is terminated while the flow of dry nitrogen is continued, whereupon any excess moisture on the face of the film will be dissipated and the adsorbed moisture will remain in the hygroscopic film. After a few seconds of flow of the dry nitrogen film alone, the flow of anhydrous hydrogen fluoride gas is commenced as to start the etching phase. The flowing anhydrous hydrogen fluoride gas reacts with the moisture adsorbed in the hygroscopic film and with the oxide in the film as to remove at least a portion of the film. When an appropriate etch time has elapsed, the flow of anhydrous hydrogen fluoride is stopped while the flow of dry nitrogen is continued so as to terminate the etch and purge the processing chamber again.

The dry nitrogen flow control 32 accommodates flows within the range of 0 to 30 slm and the flow control is preferably operated in the range of 10 slm to about 20 slm. Typically, the flow control 32 is operated at approximately at fifty percent of its capacity, allowing flow of 15 slm.

The quantities of deionized water, as set forth, produce vapor, as to create humid conditions of from five to twenty-five percent relative humidity in flow line 35. Typically the humidity will be in the range of seven to ten percent relative humidity prior to entering the mixing device 36. With humidity in this approximate range, good etching results have been obtained.

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Whereas the flow control 41 which regulates the flow of anhydrous hydrogen fluoride gas, operates within the range of 0 to 1.0 slm, the flow control 41 typically operates within the range thirty percent of capacity to ninety percent of capacity, thereby allowing flows of anhydrous hydrogen fluoride gas in the range of 0.3 slm to 0.9 slm.

The etching reaction is very fast with a total amount of the silicon dioxide, polysilicon dioxide, silicon nitride or other film removed depending upon the relative concentration of hydrogen fluoride in the etchant mixture. The etch rate with the parameters herein pointed out and using anhydrous hydrogen fluoride gas on such films is in the range of 100 to 14,000 angstroms per minute. Etching at a rate of up to 5,000 angstroms per minute is highly controllable and useful.

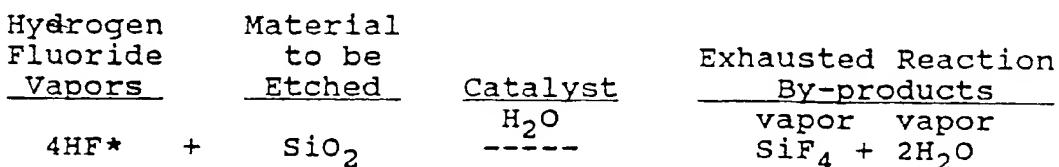
Taking into consideration that the hydrogen fluoride is thoroughly mixed in the mixing device with the moistened nitrogen gas, the concentration of the mixture of gases as the gases enter the process chamber is approximately from 15 to 300 parts of moist nitrogen by mass to 1 part of hydrogen fluoride by mass, and preferably, the concentration is approximately about 30 parts of moist nitrogen to 1 part of hydrogen fluoride by mass.

As described above, the etching process involves a pre-purge, with the dry nitrogen gas, then the actual etching of the film from wafer W while the reactive gas is flowed into and through the process chamber, and

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In the etching process of removing silicon dioxide from the face of a silicon wafer, the resultant products are and remain in vapor form. The actual etching process is very complex, being comprised of several steps. The formal mechanisms of reaction are not clear, but the experiments performed during the development of the process suggest the following explanation.

I. In the course of etching the surface, hydrogen fluoride vapors remove silicon dioxide by a chemical reaction which converts the solid  $\text{SiO}_2$  to a gaseous form, probably  $\text{SiF}_4$ .



NOTE: A descriptive sequence, not necessarily the exact chemical reaction mechanism.

Water acts as a catalyst to the reaction through formation of some intermediate.

\* This vapor could be in the form of dimer  $(\text{HF})_2$ , hexamer  $(\text{HF})_6$ , etc.

The vapor products of this reaction are swept out of the chamber by the inert gas, completing the removal of the silicon dioxide. Water vapor is needed for etch rate uniformity.

Numerous silicon wafers with silicon oxide films thereon have been etched as to remove the films from the faces of the wafers or to remove a portion of the film. Also nitride films may be etched and have a much slower

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etch rate than does silicon dioxide, at approximately ten percent of the silicon oxide etch rate.

The portions of the films which have been removed have been measured by state-of-the-art apparatus familiar to persons of skill in this art and measured in angstroms. In all of the examples hereafter described, the flow controller regulating the flow of anhydrous hydrogen fluoride gas was maintained to a temperature sufficient to prevent condensation of hydrogen fluoride gas, or about 43°C; and the hydrogen fluoride source was similarly heated to create hydrogen fluoride vapor and avoid any hydrogen fluoride condensation in the flow lines. Also, the process chamber was continuously opened to vent to maintain a near normal atmospheric pressure in the process chamber; and no heat was added to the process chamber, apart from the gases being flowed into it.

In the etching process, the etchant mixture flows through the process chamber 12 and is vented through the exhaust 13 which remains open to the atmosphere or slightly throttled to slightly increase pressure in the process chamber. The present process realizes extremely high etch rates so that no holding time of the etchant mixture in the process chamber 12 is required to complete the process. After the charging of the process chamber 12 is complete, valves 47 and 28 are closed while the flow of dry nitrogen continues to flow through the system, purging lines 24, 25 and 43, vapor chamber 41, mixing chamber 50 and process chamber 12 of the etchant mixture.

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EXAMPLE I

In this example, silicon wafers with silicon oxide films were etched in the process wherein all of the parameters were held constant excepting the flow rate of anhydrous hydrogen fluoride gas which was progressively increased, thereby progressively increasing the concentration of the anhydrous hydrogen fluoride gas applied to the wafers. Flow of dry nitrogen was held at 15 liters per minute; 1 cc of deionized water was injected into the vapor chamber for each wafer processed; the vapor chamber was held at 120°C; and the nitrogen sweep through the vapor chamber was a rate of 0.8 liters per minute. With this rate of water injection and sweep through the vapor chamber, approximately nine percent relative humidity in flow line 35 is experienced. The wafer was rotated at six r.p.m. It was observed through the use of transparent flow lines from the vapor chamber, that sufficient vapor was available so that vapor was supplied into the gas mixture for the process chamber all during the flow of anhydrous hydrogen fluoride gas in each cycle. Process chamber pressure was at or slightly above atmospheric pressure by a small amount caused by producing continuous flow through the chamber. The vent was not intentionally throttled. Etch time or duration of the flow of the anhydrous hydrogen fluoride gas was maintained at 8 seconds per wafer etched. The following TABLE I of twenty-four etch cycles demonstrates the controllability and repeatability of the etching as disclosed.

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TABLE I

FILM THICKNESS

<u>HF Flow Rate, l/min.</u>	<u>Initial Thickness Angstroms</u>	<u>Average Removal x</u>	<u>Standard Deviation In Removal s</u>
0.50	4948 4630 4274 4905 4496 4143	365.17	33.75
0.55	4844 3979 3389 4836 4178 3699	648.17	127.36
0.75	4827 3864 4823 3710	1077.75	86.55
0.85	4827 3612 4820 3452	1330.75	77.17
0.90	5057 3623 4920 3472	1435.50	24.41

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EXAMPLE II

In this example all of the parameters of the etching processes were maintained constant with the exception of the time of the etch. The nitrogen flow rate was maintained at 15 liters per minute; the flow rate of the anhydrous hydrogen fluoride gas was maintained at 0.5 liters per minute; water was metered into the vapor chamber at a rate of 1 cc of deionized water per etching cycle, i.e. for each wafer; the vapor chamber was maintained at 120°C; and the sweep of nitrogen through the vapor chamber was maintained at a rate of 0.8 liters per minute. The wafer was revolved at a rate of six r.p.m. It was observed, through the use of transparent flow lines from the vapor chamber that sufficient vapor was available so that vapor was supplied into the gas mixture for the process chamber all during the flow of anhydrous hydrogen fluoride in each cycle.

Table II reports results of twenty-seven etching cycles, and demonstrates the controllability and repeatability of the process.

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TABLE II

FILM THICKNESS

<u>Etch Time Seconds</u>	<u>Initial Thickness Angstroms</u>	<u>Average Removal X</u>	<u>Standard Deviation In Removal S</u>
8 sec.	4948 4630 4274 4905 4496 4143	365.17	33.17
12 sec.	5032 4061 3078 1971 5004 3936 2885	1039.14	47.55
16 sec.	4959 3406	1562.50	13.44
20 sec.	4941 2933	2012.50	6.36
25 sec.	4926 4914 4901	2586.00	82.93
30 sec.	4913 4875 4875 4870 4860 5581 5565	3301.29	103.79

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EXAMPLE III

In this Example the amount of oxide film or removal was measured at five places on each wafer, at the center, and adjacent the edge at four locations approximately equally spaced about the periphery, referred to as a top, middle, bottom, left and right. All of the parameters were maintained constant, a series of wafers were etched and the film removal at the five locations on each wafer was measured. The flow control for the anhydrous HF gas was adjusted to fifty percent of capacity, or 0.5 slm. The etch continued for 12 seconds; the water vapor continued for 12 seconds; the anhydrous HF source bottle was heated to 30°C; the anhydrous HF gas flow control was heated to 40°C; the dry nitrogen flow control was adjusted to fifty percent capacity or 15 slm; and the nitrogen sweep through the vapor chamber was adjusted to forty percent, or 0.8 slm. Vapor flow continued all during flow of anhydrous hydrogen fluoride gas. Table III demonstrates the controllability, repeatability and uniformity of the etchant various locations on the faces of the wafers.

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TABLE III  
FILM THICKNESS

<u>Wafer Number</u>	<u>Initial Thickness Angstrom</u>	<u>Average Removal x</u>	<u>Standard Deviation In Removal s</u>
1	4992(T) 4915(M) 4901(B) 4914(L) 4890(R)	739.80	19.92
2	4268(T) 4178(M) 4132(B) 4194(L) 4141(R)	680.40	36.07
3	3649(T) 3486(M) 3418(B) 3510(L) 3448(R)	759.80	45.03
4	2965(T) 2705(M) 2615(B) 2744(L) 2685(R)	734.80	12.05
5	2244 1966 1868 2000 1962	714.20	37.06
6	8435(T) 8336(M) 8357(B) 8185(L) 8176(R)	630.80	99.07
7	7746(T) 7633(M) 7645(B) 7689(L) 7622(R)	635.80	62.31
	7125(L) 6905(R)		

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ADDITIONAL EXAMPLES

Extremely rapid removal of the oxide film was experienced when anhydrous hydrogen fluoride gas was used without the diluent nitrogen gas, but with the nitrogen sweep through the vapor generator at a rate of 0.6 to 0.7 slm with the amount of water vapor produced by a spray of at least 0.3 cc of deionized water per operational cycle, or per wafer. The oxide was removed from the wafer shortly after 3 seconds of etch time, in the amount of 5,000 to 6,000 angstroms of thickness. The temperature of the anhydrous hydrogen fluoride gas supplied to the process chamber was approximately 40°C at the flow control.

In another example, wafers with doped film, exhibiting hydroscopic characteristics and with moisture absorbed into the film, were etched with a concentration of ten to fifteen percent anhydrous hydrogen fluoride gas to diluent dry nitrogen gas, but without any added vapor. The etch time was 20 to 30 seconds and in excess of 1,000 angstroms were stripped from the wafer.

In still another example with flow control 33 set at twenty-five percent for a 0.5 slm nitrogen flow, and flow control 32 set at fifty percent for a 15 slm flow of dry nitrogen, and vapor generated to establish seven percent relative humidity in flow line 35, good etching results were obtained with flows of anhydrous hydrogen fluoride in the ranges previously set forth.

Likewise satisfactory etch results were obtained when flow rates were changed to 0.6 slm nitrogen sweep through the vapor chamber, 15 slm dry nitrogen and seven percent relative humidity measured at line 35, together with ranges of flow of anhydrous hydrogen fluoride as previously set forth.

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In another example, the throttle valve 13.1 was adjusted to restrict flow to the vent and thereby increase pressure in the process chamber to about 23 inches of water, and with the ratios of flow of nitrogen to flow of anhydrous hydrogen fluoride gas in the range of 35 or 40 to 1, vapor generated by bubbling gas through an unheated water bath and producing a relative humidity of 22 to 23 percent in the combined gases entering the process chamber, etch rates of approximately 3000 angstroms in 18 seconds, or about 10,000 angstroms per minute were achieved.

The wafer W which has been subject to the etching process is illustrated in FIGS. 2 and 3. The original face F of the wafer is indicated in dashed lines. The substrate 8 of the wafer may be of any of the materials indicated, but most often is of silicon. The etchable film 9 on the substrate may be partially removed by the etch as illustrated in FIG. 2 to define a new face 9.1 or the film 9 may be entirely removed by the etch as to expose the face 8.1 of the substrate. As pointed out above, the surfaces 8.1 and 9.1 are smooth upon completion of the etch, without damage or roughening of the surface due to the etch; and there is an increased level of free fluorine atoms on surfaces 8.1 and 9.1 after completion of the etch. Furthermore, in geometry etching, narrow line widths will be formed.

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That Which Is Claimed Is:

1. A process of removing at least a portion of a film from a substrate, comprising exposing the substrate to a hydrogen halide gas and to moisture, characterized in that flowing anhydrous hydrogen halide gas and moisture are supplied from separate controlled sources and react with each other in removing a portion of the film, and continuously flowing dry inert diluent gas over the substrate and film before, during and after exposing the substrate to the flowing anhydrous hydrogen halide gas.
2. A process according to claim 1 characterized in that said gas is anhydrous hydrogen fluoride gas.
3. A process according to either of claims 1 or 2 characterized in that the moisture is applied as a flowing vapor simultaneously with, but from a separate source than the anhydrous hydrogen fluoride gas.
4. A process according to either of claims 1 or 2 characterized in that the film is hygroscopic, the moisture having been adsorbed by the film prior to application of the anhydrous hydrogen fluoride gas.
5. The process according to either of claims 1 or 2 characterized in that the exposing of the substrate and the inert gas are at near room temperature.
6. A process according to either of claims 1 or 2 characterized in that the exposing of the substrate is at near normal atmospheric pressure.

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7. A process according to either of claims 1 or 2 characterized in that the exposing of the substrate is carried out under pressure conditions of up to thirty-five inches of water.

8. A process according to claim 3 characterized in that the vapor is flowed over the substrate prior to exposing the substrate to the anhydrous hydrogen fluoride gas to pretreat the film.

9. A process according to claim 8 characterized in that the vapor is flowed over the substrate continuously during the pretreating and all during exposure of the substrate to the anhydrous hydrogen fluoride gas.

10. A process according to claim 3 characterized in that flows of anhydrous hydrogen fluoride gas and of vapor are terminated substantially simultaneously to stop the removal of film.

11. A process according to claim 4 characterized in that moisture is applied as a vapor flowed over the substrate prior to but discontinued during exposing the substrate to the anhydrous hydrogen fluoride gas.

12. A process according to either of claims 1 or 2 and discontinuing the flow of anhydrous hydrogen fluoride gas while continuing the flow of diluent inert gas to stop the removal of film.

13. A process according to either of claims 1 or 2 characterized in that the inert gas comprises dry nitrogen.

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14. A process according to either of claims 1 or 2 characterized in that the substrate comprises an article with film on numerous faces thereof.

15. A process according to claim 3, characterized in that a plurality of substrates are exposed simultaneously to said anhydrous hydrogen fluoride gas in presence of said dry diluent inert gas.

16. A process according to claim 3 characterized in that the water vapor is carried by inert gas to the anhydrous hydrogen fluoride gas to establish the presence of water vapor therein.

17. A process according to either of claims 1 or 2 characterized in that the exposing of the substrates continues for a time period within the range of five seconds to thirty seconds.

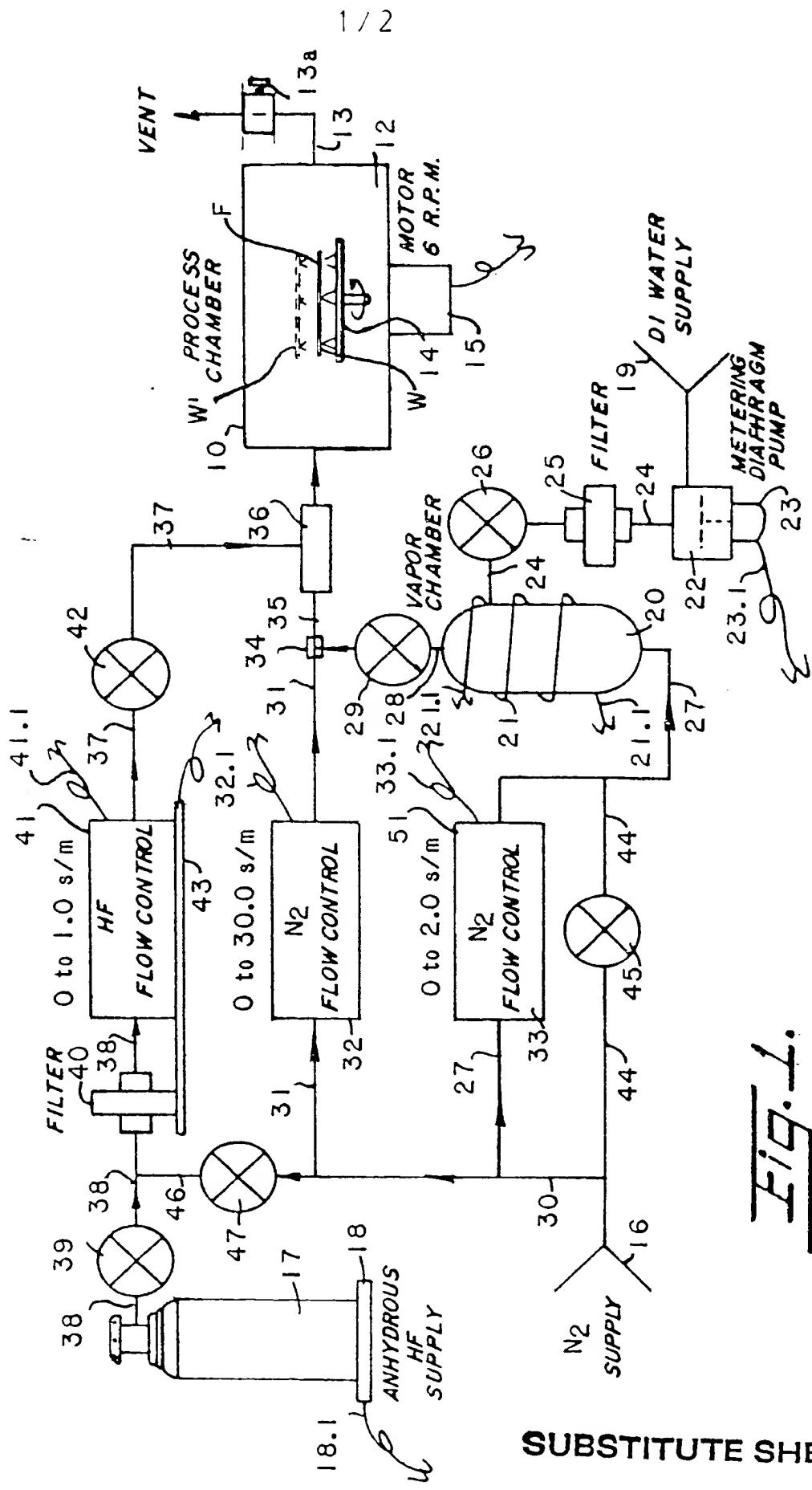
18. A process according to either of claims 1 or 2 characterized in that the relative proportions of anhydrous hydrogen fluoride gas and dry diluent inert gas are varied to change the rate of removal of the film.

19. A process according to either of claims 1 or 2 characterized in that the substrate is revolved while exposing of the substrate continues.

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20. Apparatus for processing a substrate for removing film therefrom, comprising a process chamber to confine the substrate and having a vent open to atmosphere, characterized in that a gas mixing means is connected in fluid communicating relation to the process chamber for supplying mixed gases into the process chamber, a first source of anhydrous hydrogen fluoride gas having connection to the gas mixing means, a second source of dry inert gas, a third source of water vapor, means connecting the second and third sources to the gas mixing means for mixing inert gas and water vapor with anhydrous hydrogen fluoride gas and to be delivered therewith into the processing chamber to produce reaction with the film on the substrate.

21. Apparatus for processing a substrate according to claim 20 characterized in that the source of water vapor has a bath of water and flow means directing inert gas over the bath.



SUBSTITUTE SHEET

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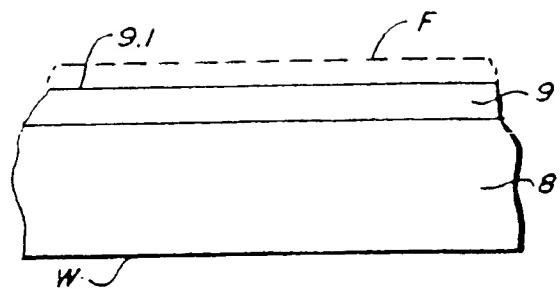


Fig. 2.

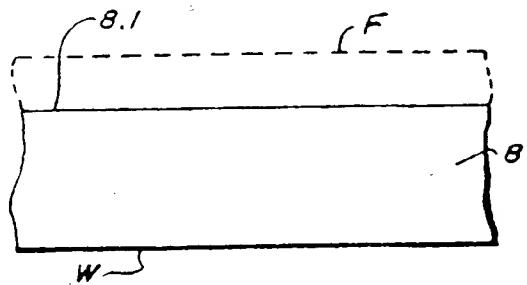


Fig. 3.

# INTERNATIONAL SEARCH REPORT

International Application No. PCT/US 86/01714

## I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) \*

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC<sup>4</sup>: H 01 L 21/306

## II. FIELDS SEARCHED

Minimum Documentation Searched \*

Classification System	Classification Symbols
IPC <sup>4</sup>	H 01 L

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in the Fields Searched \*

## III. DOCUMENTS CONSIDERED TO BE RELEVANT\*

Category *	Citation of Document, if with indication, where appropriate, of the relevant passages **	Relevant to Claim No. ***
A	DE, A, 1041164 (LICENTIA) 16 October 1958, see column 4, line 67 - column 5, line 55 --	1, 2, 5, 6
A	IBM Technical Disclosure Bulletin, volume 19, no. 7, December 1976, (New York, US) K.D. Beyer et al.: "Etching of SiO <sub>2</sub> in gaseous HF/H <sub>2</sub> O", page 2513, see page 2513, paragraph 1 --	1, 2, 5, 6
A	IBM Technical Disclosure Bulletin, volume 22, no. 7, December 1979, (New York, US), K.D. Beyer et al.: "Removal of native oxide layer on a semicon- ductor surface", page 2839, see page 2839, paragraphs 1-3 --	1, 2, 5, 6
A	US, A, 3773578 (W.B. GLENDINNING et al.) 20 November 1973, see claims 1, 2 --	1, 2, 5, 6
A	Patents Abstracts of Japan, volume 5, no. 159 (E-77) page 831, 14 October 1981, & JP, A, 56-88320 (FUJITSU) 17 July 1981	1, 2, 5, 6

\* Special categories of cited documents:   
"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date  
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means  
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search

5th February 1987

Date of Mailing of this International Search Report

09 MAR 1987

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer